Rheological model of semi-solid A356–SiC composite alloys. Part I: Dissociation of agglomerate structures during shear

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Abstract

This study investigates the rheological behavior of semi-solid A356 alloys reinforced with SiC particles of 10–15 μm. The interaction between the primary phase and the reinforcing particles plays a major role in characterizing the thixotropic nature of these alloys. Viscosities were determined using a Couette type viscometer by measuring the torque on a calibrated spindle rotating in a cylindrical alumina crucible containing the alloy composite. The thixotropic behavior of these composites was described by an analytical model where the dissociation of the primary phase particle structure is expressed in terms of a structural parameter $\lambda$, which depends on shear rate, duration of shear and effective solid fraction. The analytical model was applied successfully to the results of this study as well as to the results of similar studies in the literature. Observations showed that the kinetics of dissociation of this structure is strongly influenced by increasing shear rate, and decreasing fraction of primary solid phase. It was also demonstrated that the effective solid fraction composed of agglomerates of primary particles with entrapped liquid alloy has a larger influence than the form factor or mean particle size. The presence of reinforcing particles was found to oppose the tendency of primary particles to agglomerate so that the kinetics of dissociation of the particle structure is enhanced.

Keywords: Shear; Silicon carbide; Solidification

1. Introduction

Mechanical stirring of an alloy during solidification has been shown to change the structure of the solidified phase from dendritic to more or less spherically shaped particles. The morphological characteristics of the solidified material depend on the solid fraction, the rate of shear and on the solidification rate [1–6]. Stirring in the semi-solid state reduces the apparent viscosity considerably and facilitates the shaping of these alloys into a final form [7–11]. It has been observed that forming techniques normally used for solid alloys require considerably less energy to achieve the desired shape [12] when the alloy or composite is in the semi-solid state.

An important consideration of processing particulate reinforced semi-solid alloys is the difficulty of incorporating the particles into the alloy. It has been reported that they are much more easily incorporated in the semi-solid state [13–16] when compared with other techniques of fabrication of metal-matrix composites. Powder metallurgy or infiltration techniques are less efficient, making this a preferred technique for large volume applications.

In order to optimize the semi-solid processing of these alloys, the rheological characteristics must first be characterized in terms of constitutive equations. The presence of reinforcing particles in semi-solid alloys, however, add an additional degree of complexity to these systems in that two solid phases with different properties are involved. The analytical formulation of the deformation behavior must take into account the external variables which can be controlled, such as temperature, shear rate, shear stress, duration of shear and the volume fraction of the reinforcing particles. These variables define the size and shape of the solidifying primary phase particles and their distribution in the final product. The particles change with time owing to dissociation or reconstitution of agglomerates resulting
from the thermomechanical processing stages of the alloy or of the composite and thus contribute to the thixotropic nature of these alloys.

A previous study [17,18] has shown that the apparent viscosity decreases as a function of the duration of shear at constant shear rate and can be described to occur in two stages as shown in Fig. 1. The viscosity decreases rapidly during the initial period of shear. This is attributed to the dissociation of agglomerates of solid particles which are weakly bonded, trapping liquid alloy within the inter-aggregate spaces. Owing to the mechanical forces of stirring, these agglomerates are dissociated, liberating the entrapped liquid which results in the apparent viscosity decrease.

During the second stage, the viscosity decreases much more slowly, eventually stabilizing to a steady state value. This occurs because the inter-particle bonds of the primary phase are much stronger than the inter-aggregate bonds. During shear, the dissociation or reconstitution of the inter-particle bonds is controlled by the mechanical stirring forces. Increased shear rate breaks up these bonds but can also increase the frequency of collision between these particles resulting in the formation of new agglomerates. With increasing stirring time, small particles tend to coalesce as a result of Ostwald ripening which tends to decrease the form factor and increase particle size. The combined effect results in a slowly decreasing viscosity. A dynamic equilibrium is eventually reached when the mechanisms of dissociation and reconstitution reach a steady state corresponding to the lowest viscosity value for a specific solid fraction and constant shear rate. The same viscosity decrease was observed by Loué et al. [16], Kattamis and Piccone [19], Moon et al. [14], and Moon [15].

An analytical model was developed [17,18] to describe the thixotropic behavior of Al–6%Si composite reinforced with SiC particles where the dissociation of the semi-solid structure changes with time. The resulting model defines a parameter $\lambda$, which characterizes the structure of the particles and agglomerates. At $t = 0$, the structure is in its most ordered state and $\lambda = 1$, whereas the structure is degraded to a value of $\lambda = 0$ at $t = \infty$.

The objective of this study is to develop the constitutive equations which can account for the thixotropic nature of semi-solid alloys and composites in terms of the structural parameter $\lambda$ and to test this model on other alloy systems in the literature where viscosities in the semi-solid state have been measured. The influence of the volume fraction of reinforcing particles, rate of shear and solid fraction of primary phase are the external control parameters that are examined.

2. Theoretical analysis

2.1. The constitutive equations and the dissociation of the structure of semi-solid alloys

Incompressible fluids, laminar shear flows, and simple unidirectional shear flow [20], can be expressed in constitutive equations which describe the time dependent behavior of non-Newtonian, inelastic fluids as follows:

$$\tau = \eta(\lambda, \dot{\gamma}) \dot{\gamma}$$  (1)

where

$$\frac{d\lambda}{dt} = g(\lambda, \dot{\gamma})$$  (2)

where the viscosity of the fluid $\eta$ is a function of the structural parameter, $\lambda$, and the shear rate, $\dot{\gamma}$. Eq. (1) represents the equation of state for flow with a constant value of the structural parameter $\lambda$ and Eq. (2) describes the kinetics of the variation of the structural parameter (i.e. its time-dependant behavior).

For cases of thixotropic behavior, the function $g$ of Eq. (2) must verify the condition

$$\left(\frac{\partial g}{\partial \dot{\gamma}}\right)_{\lambda} < 0$$  (3)

The structural parameter $\lambda$ is defined as the fraction of the melt which remains unchanged and $(1 - \lambda)$ repre-
sents the fraction which has degraded at any time $t$. This parameter can be further defined for following boundary conditions:

(a) Initial condition, at $t = 0$, $\lambda = \lambda_0 = 1$, corresponding to the state where no bonds are dissociated.

(b) Dynamic equilibrium, at $t = t_e$, $\lambda = \lambda_e$, is only a function of the rate of shear.

(c) Complete degradation, at $t = t_{oo}$ and $\dot{\gamma} = \infty$, $\lambda = \lambda_{oo} = 0$, corresponding to a complete dissociation into discrete particles.

Using the analogy of the chemical kinetics to express the rate of dissociation and reconstitution of these structural bonds we can write the Eq. (2) as

$$\frac{d\lambda}{dt} = k_1(\lambda - \lambda_e)^p - k_2(\lambda_0 - \lambda)^q$$

where $k_1$ and $k_2$ are the corresponding kinetic constants for the dissociation and the reconstitution of the structure of the semi-solid alloy. This structural parameter depends on the shear rate, temperature (solid fraction of primary phase) and on the solid fraction of the reinforcing phase. An equilibrium structure is attained for each set of specific shear conditions where $\lambda = \lambda_e$ at a constant shear rate.

It was experimentally determined [17,18] that the “reaction order” exponent $p$ is equal to 1, and that the rate of reconstitution of the structure during stirred conditions is negligible with respect to the rate of dissociation of the structure, so that ($k_1 \gg k_2$). This phenomenon was also observed by Moon et al. [14]. We can express the rate of change of the structural parameter as

$$\frac{d\lambda}{dt} = k_1(\dot{\gamma})(\lambda - \lambda_e)$$

By applying condition (a), Eq. (5) can be integrated to give

$$\lambda = \lambda_e + (1 + \lambda_e) \exp(-k_1t)$$

Lapasin et al. [21] have expressed the shear stress as a polynomial of $\lambda$ where

$$\tau = f_0(\dot{\gamma}) + \lambda f_1(\dot{\gamma}) + \cdots + \lambda^q f_q(\dot{\gamma})$$

This equation can be simplified for a large number of cases by using only the first two terms of the expression, so that:

$$\tau = f_0(\dot{\gamma}) + \lambda f_1(\dot{\gamma})$$

The variation of shear stress with time at constant shear rate is given as:

$$\left(\frac{d\tau}{dt}\right) = f_1(\dot{\gamma}) \frac{d\lambda}{dt}$$

By applying conditions (a) and (c), $\dot{\gamma} = 1$ at $t = 0$ which correspond to the maximum shear stress $\tau_0$, where:

$$\tau = \tau_0 = f_0(\dot{\gamma}) + f_1(\dot{\gamma})$$

At $t = t_e$, $\dot{\gamma} = \dot{\gamma}_e = 0$, corresponding to

$$\tau_e = f_0(\dot{\gamma})$$

Eqs. (10) and (11) therefore give

$$f_1(\dot{\gamma}) = \tau_0 - \tau_e$$

Combining Eqs. (9) and (12) gives

$$\frac{d\tau}{d\tau_e} = \left(\tau_0 - \tau_e\right) \frac{d\lambda}{d\tau_e}$$

Integrating,

$$\tau = (\tau_0 - \tau_e)\lambda + \tau_e$$

The value of the term $\tau_e$, corresponding to the shear stress of completely dissociated bonds, is much smaller than $\tau$ or $\tau_0$ and can therefore be ignored so that the structural parameter $\lambda$ is simply the ratio of the actual shear stress and the initial shear stress, and the equilibrium parameter $\lambda_e$ is defined in a similar fashion:

$$\lambda = \frac{\tau}{\tau_0} \quad \text{and} \quad \lambda_e = \frac{\tau_e}{\tau_0}$$

The constitutive equations for the dissociation can therefore be represented as follows,

$$\tau = \lambda \tau_0$$

and

$$\lambda = \lambda_e + (1 - \lambda_e) \exp(-k_1t)$$

Eq. (16) defines the behavior for constant $\lambda$, and Eq. (17) describes the dissociation of the structure $\lambda$ as a function of the duration of shear at constant shear rate. The parameter $\lambda$ depends on the combined effect of inter-aggregate bonding, inter-particle bonding, and on Ostwald ripening. Inter-aggregate bonding results in liquid entrapment and consequently increases the effective solid fraction of the composite material. The inter-particle bonds can either be broken or reconstituted while the effect of Ostwald ripening generally increases the average particle size and makes the particles more spherical in the process of minimizing the interfacial energy of the system. Consequently, the principal parameters that identify structural change are $\phi_{def}$, the effective solid fraction of the primary phase, $d_m$, the mean particle diameter, $S_v$ the form factor (area/volume), and $\phi_{Max}$, the limiting compact solid fraction. This limiting compact solid fraction corresponds to the condition where the mixture of particles and aggregates behaves like a solid and depends only on $\dot{\gamma}$.

The parameter $\lambda$ can be clearly defined in terms of the principal structural parameters by using Mori–Oto-take model [22] which defines the viscosity of a suspension of particles according to the expression:
where $\phi$ is the solid fraction of suspended particles, and $\eta_L$ is the viscosity of the liquid phase.

2.2. Semi-solid metal matrix composite alloys

For the case of semi-solid metal matrix composite alloys, two types of particles are present: (a) primary phase particles which are deformable in size and shape during shear (ranging from 100–300 μm) and (b) particles of reinforcing material such as SiC which are non-deformable (10–15 μm) and whose morphological characteristics do not change with time. The interactions of these two types of particles play a significant role in the rheological behavior of these systems.

In order to relate the structural parameter $\lambda$ to the other factors, the concept of Fidleris and Whitmore [23] was applied where a large particle falling by gravity in a suspension of fine particles smaller than one-tenth of the diameter of the large particles encounters the same resistance to flow as if the suspension were replaced by a homogeneous liquid of equivalent density and viscosity. This concept was also used by Faris [24] in order to evaluate the viscosity of multimodal suspensions. Using this same approach, where the reinforcing particles of SiC are much smaller (10–15 μm) than the primary phase particles (100–300 μm) we can write Eq. (18) in a similar form.

$$\eta = \eta_L + \frac{\eta_L S_M d_M}{2 \beta}$$

with

$$\beta = \frac{1}{\phi_{\text{eff}}} - \frac{1}{\phi_{\text{Max}}}$$

where $\eta^*$ represents the viscosity of the liquid suspension containing only reinforcing particles, $\phi_{\text{Max}}$ is the limiting compact solid fraction, and $\phi_{\text{eff}}$ is the effective solid fraction of the semi-solid composite defined by:

$$\phi_{\text{eff}} = \frac{V_p + V_{LT}}{V_p + V_L + V_R}$$

where $V_p$, $V_{LT}$, $V_L$, and $V_R$ are respectively the volume fraction of primary phase particles, the volume fraction of trapped liquid, the liquid volume fraction, and the volume fraction of reinforcing particles. If $f$ is the fraction of trapped to total liquid ($f = V_{LT}/V_L$), $\phi_{\text{eff}}$ can also be written as:

$$\phi_{\text{eff}} = (1 - f) \phi (1 - f) + f$$

where $\phi_R$ and $\phi$ are the reinforcing particle volume fraction and the primary solid fraction determined from the phase diagram at a specific temperature.

The Mori–Ototake model [22], can be applied in this case expressed in terms of the shear stress. At $t = 0$, this shear stress is:

$$\tau_0 = \eta^* (\dot{\gamma}) \bigg[ 1 + \frac{S_{c0} d_M}{2 \beta_0} \bigg]$$

At $t = t$, the shear stress is given by:

$$\tau = \eta^* (\dot{\gamma}) \frac{1 + S_{c0} d_M}{2 \beta}$$

From Eqs. (22) and (23) we can express the parameter $\lambda$ in terms of the ratio $\tau/\tau_0$ so that:

$$\lambda = \frac{\tau}{\tau_0} = \frac{\eta^* (\dot{\gamma})}{\tau_0} \frac{1 - \phi_{\text{Max}}}{S_{c0} d_M} + \frac{S_{c0} d_M}{S_{c0} d_M \beta_0}$$

(24)

with

$$\alpha = \frac{S_{c0} d_M}{\beta}$$

(25)

To illustrate the validity of this equation, we can combine Eqs. (22) and (23) so that $\lambda = (2 + \alpha)/(2 + \alpha_0)$, where $\alpha$ is equal to $[S_{dM} (1/\phi_{\text{eff}} - 1/\phi_{\text{Max}})]^{-1}$. For primary phase particles of $d_M \approx 250$ μm, $S_c$ is of the order $10^5$ m$^{-1}$ and $\phi_{\text{Max}}$ represents the limiting volume fraction of solid corresponding to the fully packed state. For cubic packing of monodisperse, nearly spherical solid particles, the maximum volume fraction solid is $\phi_{\text{Max}} = \pi/6 = 0.523$. When $\phi_{\text{eff}}$ is greater than 25%, as found in this case, $\alpha \approx 12.5$. Consequently

$$\lambda = \frac{\alpha + 2}{\alpha_0 + 2} \approx \frac{\alpha}{\alpha_0}$$

Eq. (24) then becomes

$$\tau = \eta^* (\dot{\gamma}) (1 - \lambda) + \lambda \tau_0$$

(27)

This equation is similar to the expression developed by Kumar et al. [25] for the case where the rheological behavior of the semi-solid alloy at beginning shear is described by a power law. The first term of the expression corresponds to the hydrodynamic forces required to put the dissociated particles in motion, while the second term represents the shear stress necessary to break the inter-aggregate bonds. For the case of semi-solid alloys, the second term is preponderant and the first term can be neglected.

For the case of non-reinforced semi-solid alloys, similar equations can be used. Here the volume of the particles is zero, or $\phi_R = 0$. In this case $\eta^* = \eta_L$ which is the viscosity of the liquid matrix alloy without reinforcing particles.

The constitutive equations can therefore be formulated for both the reinforced and the non-reinforced semi-solid alloys as follows:
\[ \tau(t, \gamma, \phi) = \lambda(t, \gamma, \phi) \tau_0(\gamma, \phi) \]  
\[ \lambda(t, \gamma, \phi) = \lambda_e(\gamma, \phi) \]
\[ + [1 - \lambda_e(\gamma, \phi)] \exp[-k_1(\gamma, \phi), t] \]  
(29)

and
\[ \lambda = \frac{S_{\gamma}dM_{\beta_{eff}}}{S_{\gamma_0}dM_{\beta_{eff}}} \]

Eq. (28) describes the rheological behavior of the semi-solid alloy or composite for a constant semi-solid structure and takes into account \( \tau_0 \) which is a function of shear rate only, and where \( \lambda = 1 \) for a given solid fraction. This clearly demonstrates the importance of defining the conditions at \( t = 0 \). Any experimental work thus necessitates that the thermal and mechanical stirring history is defined prior to the measurement of viscosity.

Eq. (29) represents the kinetics of the structural change of the solid-phase at constant shear rate. For this case the parameter \( \lambda_e \) is equal to \( \tau_e/\tau_0 \) and is determined from the curve which describes the state at dynamic equilibrium. The kinetic constant \( k_1 \) and its correlation to \( \gamma \) can be calculated from the \( \tau = \tau(t) \) curves obtained for different shear rates.

The third equation shows the relationship between the structural parameter \( \lambda \) and the other configurational parameters such as particle size and shape.

3. Experimental

3.1. Methodology

When viscosities of thixotropic materials are measured with varying shear rates, the constitutive equations can be determined from two types of results which consist of either transient curves [10,14–19] where \( \tau = \tau(t) \) as shown in Fig. (1), or by the analysis of "step shear test" results [10,14,15,25]. If it is assumed that the semi-solid material can be described by a power law model at \( t = 0 \), where \( \tau_0 = m\gamma^n \), and that the dynamic equilibrium state follows a similar relation where \( \tau_e = m_e\gamma^n_e \), the thixotropic behavior requires \( n \) to be larger than \( n_e \).

3.1.1. Analysis of transient curves

By combining the constitutive Eqs. (28) and (29), we can derive the following equation:
\[ \tau = m_e\gamma^n_e + (m\gamma^n - m_e\gamma^n_e) \exp(-k_1t) \]  
(30)

and since \( x/\tau_0 = \tau/\tau_0 \), the rheological parameters \( m_e, n_e, m, n, m_e \), and \( n_e \) can be obtained from the \( \tau = \tau(t) \) curves at constant shear rate. By varying \( \gamma \) we can generate curves representing \( \tau_0, \tau_e, \) and \( k_1 \) as a function of \( \gamma \), and thus evaluate the parameters \( m_e, n_e, \) and the function describing \( k_1 \) vs. \( \gamma \). Since we assume that the curve \( \tau_0 = \tau_0(\gamma) \) corresponds to a structure where \( \lambda = 1 \), it is essential that this structure is defined as the reference point for all subsequent isothermal viscosity measurements.

3.1.2. "Step change" method

This technique consists of shearing a sample at a constant shear rate \( \gamma \), to a point where a dynamic equilibrium state is reached and where the shear stress no longer changes with time. For an instantaneous increase in shear rate, the structure of the previous equilibrium state remains constant momentarily at the new shear rate but then decreases to a new value as a new equilibrium is reached. The procedure is shown schematically in Fig. 2 which represents a series of shear step measurements. An isostructural change is therefore described by the segments \( B_iA_{i+1} (i = 1, 2, 3, \ldots) \).

The equation \( \tau = \lambda_0 = \lambda m\gamma^n \) results in the generation of isostructure curves in the field of \( (\tau, \gamma) \) and each isostructure curve has an intersection with the curve \( \tau_e = \tau_e(\gamma) = m_e\gamma^{n_e} \)

which corresponds to the solution of the equation:
\[ \lambda m\gamma^n - m_e\gamma^{n_e} = 0 \]

If shear at a rate \( \gamma_2 \), is continued for a time up to the equilibrium value corresponding to \( B_1 \) in Fig. 2, and is then changed abruptly to \( \gamma_2 \) (point \( \gamma_2 \)), this change, described by the segment \( B_1A_2 \), evolives along an isostructure line \( \gamma_2 \), and corresponds to a shear step \( \tau_\text{step} \) which can be determined by using the first of the constitutive equations.

\[ \tau_\text{step}(\gamma_2) = \lambda_2\tau_0(\gamma_2) \]  
with \( \lambda_2 = \frac{\tau_0(\gamma_1)}{\tau_0(\gamma_2)} \)  
(31)

and therefore,
\[ \tau_\text{step}(\gamma_2) = m_e\gamma^{n_e}(\frac{\gamma_2}{\gamma_1})^n \]  
(32)

The evolution of \( \tau(t) \) from point \( A_2 \) to \( B_2 \) corresponds to the time dependent structural change at constant shear rate \( \gamma_2 \) and can be determined by combining the expression with the two previous Eqs. (28) and (29) so that:
\[ \tau(t) = m_e\gamma^{n_e} + [m\gamma^n - m_e\gamma^{n_e}] \exp(-k_1t) \]  
(33)

which is analogous to:
\[ \tau = \tau_e + (\tau_\text{step} - \tau_e) \exp(-k_1t) \]  
(34)

The parameters of these equations can be determined by using the following procedure:

1. Values of \( m_e \) and \( n_e \) of the equilibrium curve are calculated from \( \tau_e \) as a function of \( \gamma \), which requires measurements for different shear rates.
by point \( A_2 \). The same experiment is repeated at the same shear rate \( \dot{\gamma}_1 \) until point \( B_1 \) is again attained, after which an abrupt new shear rate, \( \dot{\gamma}_0 \), is applied where \( \dot{\gamma}_0 < \dot{\gamma}_1 \). This change is represented by point \( A_1 \). The results give the values of the shear stress immediately after the shear rate is changed to a new value (\( \dot{\gamma}_2 \) or \( \dot{\gamma}_0 \)). In the limiting case for an instantaneous change, it can be assumed that this represents a constant structure of the composite, which corresponds to the change of conditions represented by segments \( A_2B_1A_1 \) in Fig. 2.

The value of \( n \) can therefore be determined by the expression

\[
\frac{\tau_2}{\tau_0} = \left( \frac{\dot{\gamma}_2}{\dot{\gamma}_0} \right)^n
\]

It should be noted that a rapid change from \( \dot{\gamma}_1 \) to \( \dot{\gamma}_0 \) results in a rheopectic behavior (increase in viscosity with time at constant \( \dot{\gamma} \)), eventually reaching an equilibrium value.

(3) To obtain the value of the kinetic constant \( k_1 \), Eq. (33) can be used in the form:

\[
\ln \left[ \frac{\tau(t) - m_2 \dot{\gamma}_2^n}{m_1 \dot{\gamma}_1^n} \right] = -k_1(\dot{\gamma}_2)t
\]

where \( \dot{\gamma}_1 \) and \( \dot{\gamma}_2 \) correspond to the shear rate before, and after the step change. Since we know the experimental value of the change of \( \tau \) with time for the new shear rate, \( \dot{\gamma}_2 \), the repetition of experiments with a change in shear rate (\( \dot{\gamma}_1 \) and \( \dot{\gamma}_2 \)) can generate the value of \( k_1 \) as a function of \( \dot{\gamma} \).

3.2. Experimental apparatus and procedure

An aluminum–silicon alloy (A356) was used as the matrix material in this study which consists of 6.98 Si, 0.37 Mg, 0.10 Fe and 0.005 Cu in wt.% and is reinforced with 10–15 \( \mu \)m size SiC particles. Specific quantities of reinforcing particles of 10, 15 or 20 vol.% were added to the matrix alloy. Two different solid fractions of primary phase were chosen at 16 and 26 wt.% which correspond to alloy composite temperatures of 609 and 604 °C as determined by the Scheil equation for an Al–7.0 Si alloy [15]. The differences in solid fraction owing to the other constituents were considered to be negligible.

The experimental apparatus for measuring viscosities is shown in Fig. 3. It consists of a Brookfield viscometer fitted with a spindle fabricated from an alumina rod to which were fixed four blades (1.5 cm x 1.9 cm high and 0.40 cm thick) of zirconia using alumina cement. The spindle was sintered at 1200 °C for 6 h before use. The alloy composite was contained in a 5 cm diameter alumina crucible 12 cm high and placed in the temperature controlled zone of an electric resistance furnace. A stream of Argon was used to prevent surface oxidation.
The calibration of the viscometer was carried out according to the method of Metzner and Otto which was described in detail in previous publications [17,18].

The experimental procedure can be described in the following steps.

1. The temperature of the composite alloy was first raised to a value above the liquidus and then stirred at 40 rpm while slowly decreasing the temperature to a value corresponding to the specific solid fraction. The melt was then stirred for an additional 15 min at the same speed in order to allow the primary particles to reach an equilibrium shape.

2. After stirring, the sample was allowed to stand at constant temperature for a period of 20 min. This sequence of operations fixes the reference state of the composite and each sample was prepared in the same manner. A new sample was used for each different shear rate and solid fraction.

3. The sample was stirred at constant temperature \((T = 609 °C, \phi = 16\%)\), and at a fixed shear rate until an equilibrium state is reached as determined by viscosity measurements taken as a function of time. The same steps were repeated for each new sample sheared at a different shear rate.

4. The same procedure was also followed for the second solid fraction \((\phi = 26\%, T = 604 °C)\).

5. Also, the same procedure was followed for samples of different SiC content (10%, 15% and 20%) for each constant primary phase fraction.

4. Results and discussion

4.1. Influence of the structural parameters on the degradation of the semi-solid structure

The parameter \(\lambda\) takes into account the structural changes that occur during shear as a result of the evolution of the dimensionless form factor \(S_\lambda/S_{\lambda o}\), the dimensionless mean particle parameter \(d_{\lambda}/d_{\lambda o}\), and the factor \(\beta_\lambda/\beta_o\). Intuitively, \(\beta_\lambda/\beta_o\) should have strongest influence since this factor depends directly on the hydrodynamic forces that act on the particle bonds. The number of these bonds increases with decreasing hydrodynamic forces whereas the other two factors \((S_\lambda/S_{\lambda o}\) and \(d_{\lambda}/d_{\lambda o}\)) are mutually interdependent, and evolve continuously according to the thermodynamic driving forces resulting from the minimisation of the surface energy. The effect of the hydrodynamic forces on these two factors is limited only to the fact that convective mass transport increases with increased shear rate. The thermodynamically driven change from a dendritic to a rosette shape is relatively rapid initially and slows down when the particles become more and more spherical. Since the viscosity measurements are generally initiated at a moment when the particles approach the globularized shape, we can neglect this effect, particularly during the very rapid viscosity change in the first stage. To illustrate this effect, the data of Kattamis and Piccone [19] show that the evolution in time of the \(S_\lambda/S_{\lambda o}\) ratio for the Al–4.5 Cu–1.5 Mg alloy (Figs. 4(a) and (b)) varies only between 0.60 to 0.75 for primary solid fractions from 30% to 50%, whereas the structural parameter \(\lambda\), which was calculated by considering the viscosity change at constant shear rate, changes from 0.55 to 0.25 for the same system. This behavior is even more remarkable since the particle diameters should increase with respect to time owing to Ostwald ripening, and clearly shows that the change in effective solid fraction (primary particles plus entrapped liquid) is almost solely responsible for the rapid decrease in the viscosity during the initial stages as a result of the liberation of the entrapped liquid phase. This observation has also been reported by Ito et al. [26] who state that the viscosity is very strongly influenced by the effective solid fraction which includes the entrapped liquid phase.

4.2. Comparison of experimental and calculated results

By rearranging Eqs. (28) and (29) and dividing by \(\dot{\gamma}\) we can derive an expression which results in the variation of apparent viscosity as a function of shear time for constant \(\dot{\gamma}_1\), where \(\eta_e\) is the equilibrium viscosity and \(\eta_0\) is the viscosity before shearing, so that:

\[
\eta = \eta_e + (\eta_0 - \eta_e) \exp(-k_1 t)
\]

Eq. (36) was compared with the experimental results [17,18] for the composite Al356 + SiCp, with very good agreement as shown in Fig. (5) for primary solid fractions of 16% and reinforcing fractions (SiCp) of 20% and varying shear rates. Table 1 shows the results of different experiments for different shear rates and the calculated values of the kinetic constant \(k_1\).
results are shown in Figs. 6 and 7, clearly validating the applicability of this model in describing the thixotropic nature of these systems. Table 2 shows the calculated values of the kinetic constants for the different series of results.

Since the experimental procedures used in the various studies are not the same, the kinetic constants are consequently also different. Two different procedures were used in these studies:

(a) The semi-solid alloy is sheared with decreasing temperature until the desired solid fraction of primary phase is reached. Viscosity measurements are then taken. Moon [15] and Loué et al. [16] used temperature decrease rates of 0.075°C s⁻¹ and 0.020 °C s⁻¹ respectively.

(b) A second procedure adopted by Moon [15] consists of shearing the alloy at 900 s⁻¹ until a solid fraction of 40% is reached. The sample is then allowed to stand at rest under isothermal conditions for 30 min and subsequent viscosity measurements are then taken.

The differences reported in the table show that, for the same experimental procedure, the kinetic constant for the Al–4.5Cu–1.5Mg alloy is much greater than for the Al–7Si–0.3Mg alloy, for similar solid fraction and shear rates. This is attributed in part to a higher diffusion coefficient of copper as compared with silicon, resulting in a more rapid globularization of the primary particles in the Al–Cu alloy.
Table 1
Values of kinetic constants for different conditions for this study

<table>
<thead>
<tr>
<th>( \gamma ) (s(^{-1}))</th>
<th>( k_1 \times 10^{-3} ) (s(^{-1}))</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>16% primary solid phase</td>
</tr>
<tr>
<td>20% SiC</td>
<td>15% SiC</td>
</tr>
<tr>
<td>30.42</td>
<td>6.17</td>
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<td>12.17</td>
<td>5.67</td>
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<tr>
<td>6.08</td>
<td>5.15</td>
</tr>
<tr>
<td>3.04</td>
<td>3.87</td>
</tr>
</tbody>
</table>

Table 2 also indicates that, for results using experimental procedure (a), the kinetic constants for Al–6.5 Si and Al–7.5Si–0.3Mg are comparable. However, the comparison of the two procedures for the case of the Al–6.5Si alloy shows that procedure (b), which includes the rest period, results in a higher value of the kinetic constant. This is attributed to the longer period of time of mixing at constant temperature and at constant shear rate followed by the isothermal rest period. Rapid globularization of the primary particles is owing to Ostwald ripening which is enhanced at higher shear rates, coupled with the dissociation of agglomerated particles. In opposition to this effect, the rest time essentially causes a reconstitution of the primary particles by forming inter-aggregate bonds. In terms of the structural parameter \( \lambda \), the ratio \( S_v d_M/S_v d_M \) varies little for extended isothermal periods because of the longer rest times required in the second procedure (b). In the first procedure this parameter has a much greater influence because the alloy is not allowed to rest after shear, resulting in a much smaller quantity of entrapped liquid and which results in particles which are much less spherical. For the case of the inter-aggregate bonds which remain unaffected by the hydrodynamic forces, the kinetics are also controlled by strength of the inter-particle bonds, and the growth and coalescence of these particles. The kinetics of the dissociation of agglomerates is therefore slower and is controlled by the...
Table 2
Values of kinetic constants of different semi-solid alloys as a function of experimental conditions

<table>
<thead>
<tr>
<th>Procedure I</th>
<th>Procedure II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-4.5%Cu-1.5%Mg</td>
<td>Al-6.5%Si</td>
</tr>
<tr>
<td>γ = 200 s⁻¹</td>
<td>γ = 160 s⁻¹</td>
</tr>
<tr>
<td>Al-7%Si-0.3%Mg</td>
<td>Al-6.5%Si</td>
</tr>
<tr>
<td>φ = 0.4</td>
<td>φ = 0.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>φ</th>
<th>k₁ (10⁻³ s⁻¹)</th>
<th>φ</th>
<th>k₁ (10⁻³ s⁻¹)</th>
<th>γ (s⁻¹)</th>
<th>k₁ (10⁻³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>5.10</td>
<td>0.2</td>
<td>0.564</td>
<td>27</td>
<td>0.516</td>
</tr>
<tr>
<td>0.4</td>
<td>3.85</td>
<td>0.3</td>
<td>0.472</td>
<td>54</td>
<td>0.640</td>
</tr>
<tr>
<td>0.5</td>
<td>3.02</td>
<td>216</td>
<td>0.692</td>
<td>108</td>
<td>2.243</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>216</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4980</td>
</tr>
</tbody>
</table>

combined effect of particle growth and coalescence. This observation also shows that the term $\beta_0/\beta$ is largely responsible for the rapid dissociation of the structure of the inter-aggregate bonds which are reconstituted after long rest periods. However, if we consider the second procedure and compare the degradation of the structure with increasing rest time (Table 2), we will observe a decrease of the kinetics of degradation. This observation is owing to the increase in inter-aggregate bonds for increased rest time, which necessitates a long period to reach an equilibrium structure at constant shear rate. Fig. 8 shows the difference in procedures as expressed by the result of Moon [15] and of Loué et al. [16], expressed in terms of a dimensionless viscosity decrease.

Fig. 8. Comparison of the kinetics of degradation of semi-solid structure for Al-7Si-0.3Mg and Al-6.5Si alloys using different measurement procedures (data of Loué et al. [16] and of Moon [15]).

Fig. 9 shows the experimentally measured viscosities of the present study for primary solid fraction of φ = 16% and with $\phi_{SiC} = 20%$ at the beginning of shear (λ = 1), and at the equilibrium value (λ = λₑ), as a function of shear rate. These results clearly demonstrate that the semi-solid composite is pseudoplastic at equilibrium and at the initial condition, and that a power law ($η = mγ^n$) relationship can be used to describe this behavior. The constant m is a measure of the consistency of the fluid, and the exponent n is a measure of the degree of non-Newtonian behavior. The greater the departure from unity the more pronounced are the non-Newtonian properties of the fluid. More complete results are given in Table 3. These show that

Fig. 9. Effect of shear rate on viscosity for A356-20%SiCp alloy with 26% primary solid fraction at initial and equilibrium time of shear.
Table 3
Parameters \( n \) and \( m \) for the power law equation for initial \((t = 0)\) and equilibrium time of shear for semi-solid A356 + 20% SiC alloy

<table>
<thead>
<tr>
<th>( \phi_{\text{SiC}} )</th>
<th>( \phi = 26% )</th>
<th>( \phi = 16% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_r )</td>
<td>( \eta_0 )</td>
<td>( \eta_r )</td>
</tr>
<tr>
<td>20</td>
<td>0.010</td>
<td>18.31</td>
</tr>
<tr>
<td>15</td>
<td>0.145</td>
<td>11.53</td>
</tr>
<tr>
<td>10</td>
<td>0.276</td>
<td>7.29</td>
</tr>
</tbody>
</table>

A composite is more “rigid” and its non-Newtonian behavior is more pronounced with increasing \( \phi \) at constant \( \phi_{\text{SiC}} \) or with increasing \( \phi_{\text{SiC}} \) at constant \( \phi \). The pseudoplastic behavior at equilibrium state was also observed in other studies for semi-solid alloys [14–16,19,27] as well as for composite alloys [10,16–18,28].

4.3. Influence of shear rate on the kinetics of degradation of the structure

The variation of the kinetic dissociation constant \( k_1 \) with \( \dot{\gamma} \) is shown in Fig. 10. This figure presents the data of Loué et al. [16] for shear rates from 27 to 216 s\(^{-1}\) and the results of this study with a variation of shear rates from 3 to 30 s\(^{-1}\) for primary solid fractions of \( \phi = 16\% \) and 26\% for Al–6.5Si alloy reinforced with 10\%, 15\% and 20\% SiC particles. The results show that the value of the constant increases with increasing shear rate when plotted as \( 1/k_1 \), vs. \( 1/\dot{\gamma} \). This fraction can be represented in the form:

\[
k_1 = \frac{\dot{\gamma}}{a + b\dot{\gamma}}
\]

where \( a \) and \( b \) are empirical constants. As can be seen from Fig. 10, the value of the kinetic constant is also much more sensitive to the primary solid fraction than to the loading of the reinforcing particles, confirming that the primary solid fraction is the predominant factor in characterizing the degradation process when very small particle sizes of reinforcing material are used.

4.4. Influence of the primary solid fraction and the concentration of reinforcing particles on the kinetics of degradation of the structure

As shown in Fig. 11, an increase of primary solid fraction \( \phi \) decreases the kinetic constant for the case of two different semi-solid alloys. The variation of the
kinetic constant determined from the data of Kattamis and Piccone [19] and of Ito et al. [26] as a function of the primary solid fraction shows a linear decrease as a function of \( \phi \). It should be noted that the shear rates for these two alloys are considerably different but the actual values of \( k_i \) are in the same range, from \( 0.2 \times 10^{-3} \) to \( 0.5 \times 10^{-3} \), comparable with the values of this study. These results confirm the similarity of behavior of their experiments for semi-solid composites with this study, but which were carried out at different shear rates. This comparison is shown in Fig. 11. The increase of the kinetic constant is the result of the increased mobility of the primary particles due to their reduced number when stirred at a constant shear rate.

The influence of the concentration of reinforcing particles (\( \phi_{SiC} \)) on the values of the kinetic constant is shown in Fig. 12 for varying shear rates. It can be observed that the kinetic constant increases slightly with decreasing reinforcing fraction. However, this effect is much less pronounced than that of the primary solid fraction, as was observed in Fig. 10. This can be attributed to fact that increasing the volume fraction of reinforcing particles reduces the number of inter-particle bonds as well as inter-aggregate bonds of the primary phase. As a result, the size and number of agglomerates decreases. This dampens the effect of the initial rapid decrease in the viscosity by slowing down the dissociation of the interparticle bonds. The variation with reinforcing particle content is essentially negligible when compared with the effect of variation of the primary solid fraction. It can therefore be concluded that the primary particles contribute to the thixotropic nature of these composites because of their variable size and tendency to form agglomerates as a function of the shear conditions.

Fig. 10 shows that the value of the kinetic constant for semi-solid alloys without reinforcing particles is smaller than the value for the composite alloy, illustrating the role of the reinforcing particles in preventing re-agglomeration of the primary phase particles. The interaction between the two types of solid particles reduces the inter-aggregate bonds and thus reduces the amount of entrapped liquid within the aggregates. Both these effects result in an increase of the kinetics of the degradation of the structure.

Fig. 13 shows the normalized viscosity data of Loué et al. [16] with and without reinforcing particles for \( \phi = 40\% \) and \( \dot{\gamma} = 108 \, s^{-1} \) compared with the data of this study for alloys with reinforcing particle fractions of 10\% 15\% and 20\% SiC and a primary solid fraction of \( \phi = 26\% \), sheared at \( \dot{\gamma} = 30.4 \, s^{-1} \). It can be observed that the reinforcing particles accelerate the kinetic degradation of the structure, resulting in a more rapid decrease in viscosity. In addition, the reinforcing particles also prevent the growth of the primary particles since they are rejected into the liquid phase region. Diffusion and convection of solute between primary particles is therefore hindered, thus slowing down the rate of re-

Fig. 12. Variation of the kinetic constant \( k_i \) as a function of SiC\(_p\) content and shear rate for A356 alloys with 16\% and 26\% solid fraction of primary phase.

Fig. 13. Comparison of the rate of degradation of the semi solid structure as a function of duration of shear for Al-7Si-0.3 Mg alloys [16] and for A356 alloys with 26\% primary solid fraction and SiC\(_p\) contents of 10\%, 15\% and 20\%. 

![Graph](image-url)
structuring. The data of Loué et al. [10] for 15% SiC are found to compare favorably with the data of this study for 10% 15% and 20% SiC, again indicating the less important effect of the variation of the reinforcing particle content of the same size range. Large reinforcing particles of a size similar to the primary particles would however be expected to have a significant influence.

5. Conclusions

A rheological model for semi-solid alloys has been proposed and tested experimentally on A356 reinforced with SiC particles. The results of this study as well as the results from the literature on similar semi-solid alloys and composites were found to fit the model, based on the Mori–Ototake concept, where a structural parameter of the solid particulate material in the liquid matrix changes with the shear conditions. The model describes the kinetics of the structural degradation of the primary solid phase particles of the alloy as a function of shear rate, duration of shear and of the solid fraction of the composite.

The thixotropic nature of these materials was confirmed experimentally using a concentric cylinder viscometer. The decrease in apparent viscosity at constant shear rate can be considered to occur in two stages resulting in an exponential decrease. Initially, the rapid decrease is the result of the break up of inter-aggregate bonds, releasing the entrapped liquid within the agglomerates. This decrease was represented analytically by an expression for the evolution of the effective solid fraction of the composite as a function of the duration of shear. The second stage of degradation of the structure is slower and is attributed to the break up of inter-particle bonds, decreasing the size of agglomerates and causing the particles to become more spherical and of a more uniform size.

The experimental results have shown that the kinetics of the degradation increase with increasing shear rate, decreasing solid fraction of the primary solid phase and decreasing volume fraction of SiC particles. It became evident that the primary solid fraction has a much larger influence on the kinetics of the degradation than the SiC concentration, confirming that the primary particle interactions are the principal mechanisms which define the thixotropic nature of these composites. In addition, it was also demonstrated that the composite is pseudoplastic in the initial condition and at the equilibrium condition for a constant shear rate.

Finally, the effect of the reinforcing particles in the composite were found to oppose the agglomeration of the primary particles which results in a more rapid degradation of the agglomerate structure as compared with the non-reinforced semi-solid alloy. The practical implications of this finding are that the reinforced alloys will require shorter stirring times as compared with non-reinforced alloys in order to achieve the desired fluidity for casting or forming.

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References


